



Surface modifications of carbon nanotube/polyacrylonitrile composite films by proton beams

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Abstract

Chemical and structural modifications induced by protons at the surface of polyacrylonitrile and carbon nanotube/polyacrylonitrile composite films are analysed by TEM, profilometry, IR and XPS. Changes induced in the film are related to the energy of incident particle and implanted dose. The irradiation of the composite films induces the emergence of the nanotubes outside of the polymer but with no increase of the surface roughness. Spectroscopic modifications in both films are globally similar, the most significant feature being a lower relative concentration of nitrogen with respect to carbon close to the surface.

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1. Introduction

The discovery of nanotubes (NTs) by Iijima [1] in 1991 attracted increasing attention due to their remarkable intrinsic properties [2–4]. The insertion of carbon nanotubes in polymer matrices are expected to lead to composites with unique properties [5]. Accordingly, many polymers are presently being investigated as host matrices for carbon nanotubes and the resulting composites are being assessed for a number of properties: physical, chemical, mechan-

ical, electrical and optical conductivity, and electrostatic charging behaviour [6]. For nanotubes mass production, new processes for example based on the transformation of polyene-containing carbon to NTs [7] or the carbonization of fine core-shell polymer microspheres [8], were reported in the literature. In the case of polymer carbonization [8], polyacrylonitrile (or PAN; $(-\text{CH}_2-\text{CH}(\text{CN})-)_x$), one of the major polymer employed for carbon fibres production, was used as carbon source.

In a previous work [9], we have reported a method to obtain homogeneously dispersed multiwalled carbon nanotubes in polyacrylonitrile films by using an ultrasonic head. Zemtsov et al.

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[10,11] studied the influence of fullerene and nanotubes on the formation of a polyconjugated system in thin polyacrylonitrile films under IR treatment. They demonstrated that fullerene or NTs play the role of redox-mediator in the electrochemical behaviour. Moreover, the presence of fullerene modified the density of the film after IR treatment which was beneficial for applications, such as electrochemical rechargeable charge-storage devices [12].

Recent experimental studies [13,14] have demonstrated that proton irradiations of polyacrylonitrile films induce specific modifications at the surface of the film. The major changes are a significant depletion of the N-containing species in the first layers and a general increase in unsaturated structures similar to the structure of a graphene sheet. Exposure to air of the irradiated films provokes the incorporation of oxygen in the outermost layer of the film. In this communication, we report the modifications induced in NTs/PAN composite films, by 5 and 10 keV proton (H^+) beams. We also study the influence of the nanotubes concentration (from 0% to 10%) in the film. The aim of this work is to show the possible influence of NTs on the reactivity of the polymer but also on the formation of novel structures.

2. Experimental

The nanotubes used in this work are multi-walled carbon nanotubes (MWNTs) produced by the catalytic decomposition method [15]. The synthesis was carried out, during 60 min, in a fixed-bed flow reactor at 700 °C. The catalyst [16] contained 2.5 wt% of cobalt and vanadium supported on zeolite NaY. Acetylene (flow: 30 ml min^{-1}) and nitrogen (flow: 300 ml min^{-1}) were used as carbon source and gas carrier, respectively. The resulting powder, contains multi-walled nanotubes, amorphous carbon, graphitic particles, zeolite and catalytic particles should be purified. After the purification steps [17], the nanotubes present a purity of more than 99 wt% [9].

The preparation of the composite films was carried out in three steps. First, a solution of

polyacrylonitrile (2.5 wt%) was obtained by dissolving PAN in dimethylformamide (DMF) at 70 °C. Then, the MWNTs were added to the solution at room temperature and mixed (2×15 min) with an ultrasonic head (Branson sonifier 250) [9]. The composite films were then obtained by dipping the substrate in that solution. The substrates were stainless steel plates mechanically and electrochemically polished to promote adhesion between the metal and the organic film. The solvent DMF trapped in the film was eliminated by soaking (3 h) the sample in acetonitrile under agitation and dried in an oven at 90 °C and at a pressure of 10^{-5} mbar. Four kinds of solutions were formed: 0%, 1%, 4% and 10% of NTs with respect to the polymer concentration.

A home-made irradiation system [18] was used for the proton bombardments of the films. Irradiations have been run with 5 and 10 keV protons with a dose of 10^{16} and 10^{17} ions cm^{-2} for each incident energy. After irradiation, the samples were brought back to the laboratory atmosphere by introducing nitrogen into the irradiation chamber. The calculated projected range [19,20] of protons of 5 and 10 keV in pristine PAN film were approximately 107 and 197 nm, respectively.

The roughness (Ra) of the film surface and its thickness were measured with a Dektak 8 profiler (Veeco instruments; Stylus: diamond; 12.5 μm). The morphology and the structure of the composite films were studied by transmission electron microscopy (TEM) with a Philips Tecnaï T10 instrument. The chemical state of the surface was characterized by X-ray photoelectron spectroscopy on an SSX-100 (monochromatized Al-K α radiation, 1486.6 eV; take-off angle: 35°) instrument. The molecular structure of the samples was assessed by infrared spectroscopy (IRRAS) at a grazing angle of 80° with a Bruker Equinox 55 instrument using a MCT detector after 512 scans at 2 cm^{-1} resolution.

3. Results and discussion

First are presented the results of a pristine PAN film and pristine composite films used as reference data. Measurements are then reported on the

samples irradiated with 5 and 10 keV proton beams.

3.1. Reference films (no irradiation)

The thickness of these pristine PAN films are reproducible and close to 450 nm. Values of the roughness (R_a) averaged over a series of samples and recorded for scan distances of 100 and 500 μm are 5 and 15 nm, respectively. These values are comparable to those obtained for the polished stainless steel substrates indicating that the films are homogeneously spread on the support.

The incorporation of MWNTs in the films do not influence the thickness of the samples. For the three nanotubes concentrations, the composite films presented the same thickness close to 450 nm. Nevertheless, for the same scan distances, the R_a values increased when the nanotubes were incorporated. For a scan distance of 100 μm , values of the R_a were 20, 37 and 57 nm for samples containing 1%, 4% and 10% in nanotubes, respectively. Those values reached 40, 54 and 60 nm, respectively, for a scan distance of 500 μm . This variation is attributed to the fact that MWNTs have a length of a few microns which are several times larger than the thickness of the film.

The survey scan XPS spectrum shown in Fig. 1a matches closely to the one measured with a Scienta ESCA300 instrument on a reference PAN film [21]. The spectrum exhibits two intense and narrow peaks at 285.5 and 399.5 eV corresponding to the C 1s and N 1s levels, respectively. The decomposition of these levels is in full agreement with reference literature data [21]. We observed also that oxygen was only present at a trace level, as shown by the very weak intensity O 1s peak centred at 532.0 eV. The relative atomic concentrations of C, N and O estimated from XPS were 77%, 21% and 2%, respectively. In the case of composite films, the survey scan XPS spectra showed the same two intense and narrow peaks at 285.5 eV (C 1s) and 399.5 eV (N 1s). Oxygen was only present at a trace level. The N 1s core level has only one component corresponding to a nitrile function. In the case of C 1s, the contribution of the nanotubes and the polymer could not be distinguished, as already mentioned in [9]. The rela-

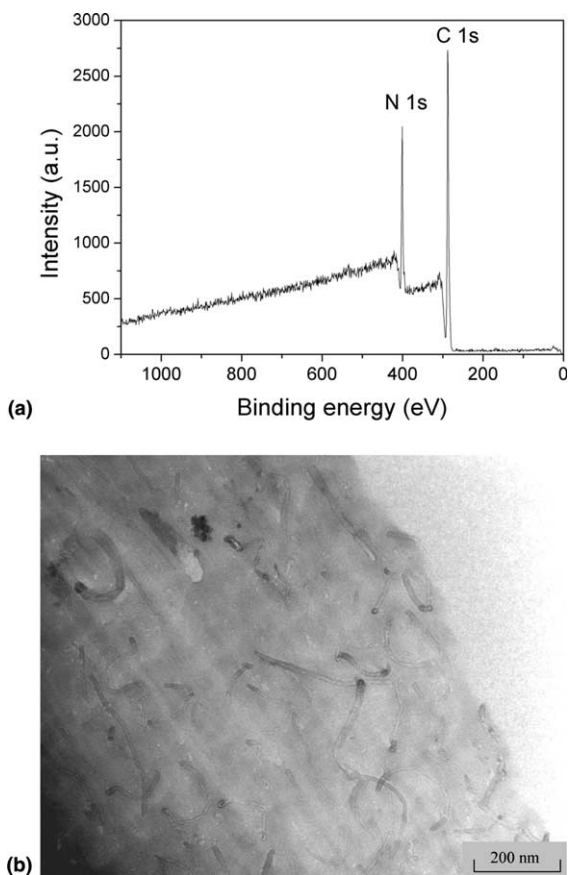


Fig. 1. (a) Survey XPS spectrum of a pristine PAN film. (b) Low resolution TEM image of the surface of composite films with 4% of nanotubes in PAN.

tive atomic concentrations of C, N and O for all the composite films were 77%, 21% and 2%, respectively. The incorporation of nanotubes in the film seems to not affect the relative percentage of these three elements at the surface.

TEM observations were only realized on composite samples. In that case, the thickness of the analysed films was around 50 μm . Fig. 1b represents low resolution TEM image of the composite film containing 4% of MWNTs. The nanotubes were homogeneously dispersed and randomly oriented into the film. Moreover, all the nanotubes were embedded into the polymer matrix. In this case, the thickness of the films was sufficient to incorporate the total length of the nanotubes. Changing the concentration of the MWNTs in the

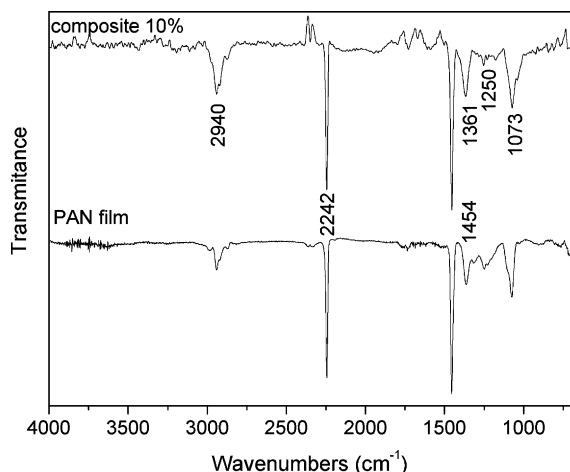


Fig. 2. IRRAS spectra of pristine PAN film and composite film with 10% of nanotubes in PAN.

films provokes only a variation of the MWNTs density. Infrared characterizations were also realized on these samples and were comparable with those obtained in previous works [13,14]. The incorporation of MWNTs in the films does not induce changes in the IR spectra (Fig. 2) as compared with a PAN film [13,14].

To sum up, both the IR and XPS characterizations of PAN and composite films were essentially identical with reference data from the literature. Modifications induced by the incorporation of nanotubes in the films cannot be detected. Only increasing surface roughness can be observed for thin films (thickness: 450 nm).

3.2. Irradiated films

Irradiations were carried out using proton beams of two energies: 5 and 10 keV. For each energy, two doses (number of implanted ions) were realized: 10^{16} at cm^{-2} and 10^{17} at cm^{-2} . Before

considering the spectroscopic results, it should be mentioned that irradiations lead to a reduction of the film thickness. This was assessed with the profiler by comparison with the film thickness in the nonirradiated zones. Table 1 shows the thickness and the Ra of the PAN and composite films after irradiation.

In the case of PAN films (without nanotubes), the thickness reduction was of the order of 60 and 100 nm, respectively, for 5 and 10 keV proton beams (dose = 10^{16} at cm^{-2}). Increasing dose does not increase erosion, the same values of the thickness are observed. Moreover, the bombardment does not increase the surface roughness. Values of the Ra were similar to those obtained for the nonirradiated PAN films. In the case of composite films, the thickness reduction seemed to disappear when the percentage of nanotubes increased in the film. With 1% of MWNTs, the reduction was comparable to that of film with no nanotubes. Irradiations were realized on composite films containing 4% of MWNTs induced on half of the erosion observed for composites with 1% of NTs. If 10% of nanotubes are present in the composite, the irradiation does not lead to a detectable film erosion. Moreover, the Ra of the films were not affected by the bombardment. We observed the same values by comparison with the Ra in the nonirradiated zones.

The survey scan XPS spectra of the PAN films irradiated with 5 keV H^+ (10^{16} at cm^{-2}) and 10 keV H^+ (10^{17} at cm^{-2}) are presented in Fig. 3a. Compared with pristine PAN (Fig. 1a), there was a large depletion of the N-containing species and a very large increase in oxygen content. Table 2 shows the relative atomic concentrations of C, N and O for irradiated PAN films.

The depletion of N-species and the increase of carbon percentage were in direct relationship with

Table 1

Thickness and surface roughness (Ra) of the PAN and composite films after irradiation

	PAN film		Comp. 1%		Comp. 4%		Comp. 10%	
	5	10	5	10	5	10	5	10
Proton beams (keV)	5	10	5	10	5	10	5	10
Thickness (nm)	390	350	390	350	420	400	450	450
Ra (nm) (scan distance = 100 μm)	5		20		37		57	
Ra (nm) (scan distance = 500 μm)	11		40		54		60	

The percentage of MWNTs in composites were: 1%, 4% and 10%.

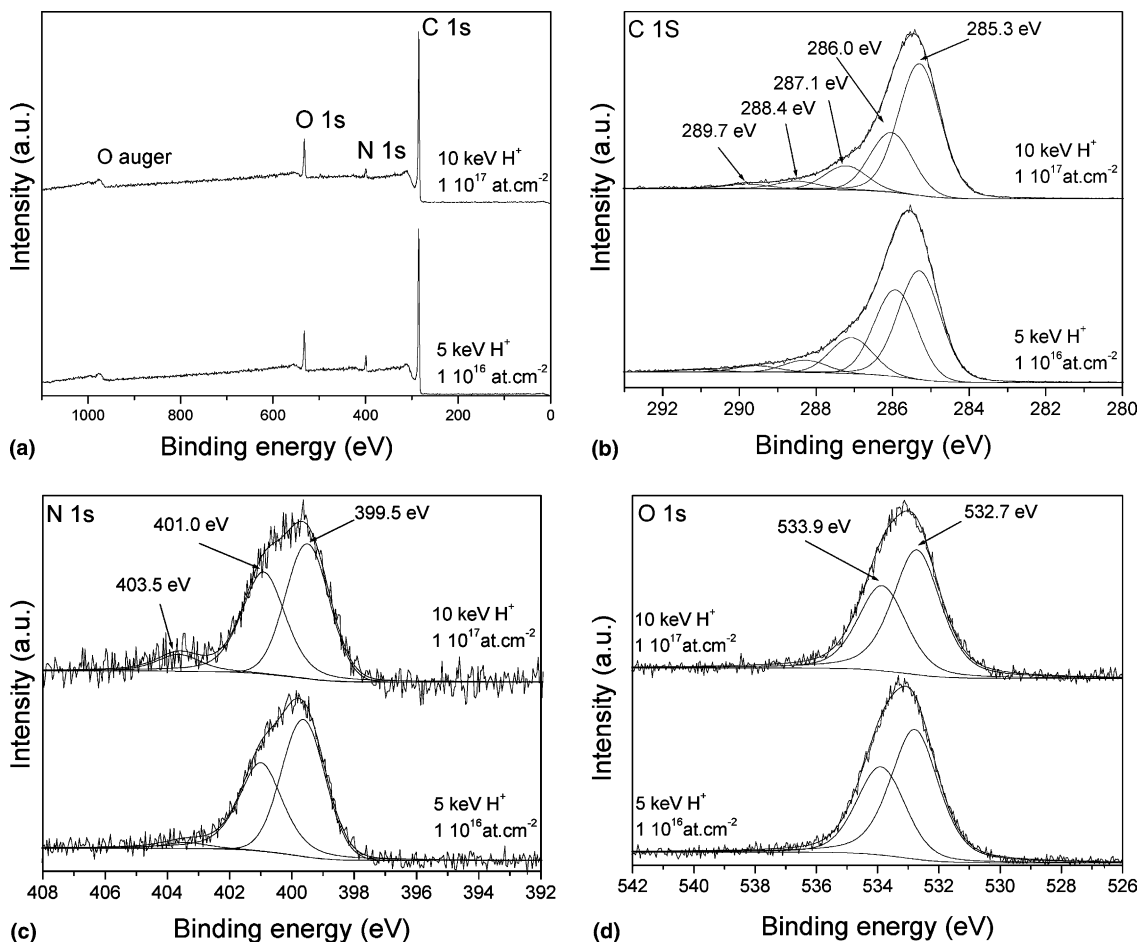


Fig. 3. Survey XPS spectra (a) and XPS spectra of the C 1s (b), N 1s (c) and O 1s (d) core levels of PAN films irradiated with 5 keV H^+ (10^{16} at cm^{-2}) and 10 keV H^+ (10^{17} at cm^{-2}).

Table 2

Relative atomic concentrations of carbon, nitrogen and oxygen for the irradiated PAN films

PAN films	Carbon (%)	Nitrogen (%)	Oxygen (%)
5 keV; 10^{16}	81	7	12
5 keV; 10^{17}	82	6	12
10 keV; 10^{16}	84	6	10
10 keV; 10^{17}	85	5	10

the increase of the incident energy and the dose. The C 1s (Fig. 3b), N 1s (Fig. 3c) and O 1s (Fig. 3d) levels spectra of the irradiated PAN films with 5 keV H^+ (10^{16} at cm^{-2}) and 10 keV H^+

(10^{17} at cm^{-2}) were presented in Fig. 3. The C 1s levels can be decomposed into five contributions appearing at 285.3, 286.0, 287.1, 288.4 and 289.7 eV. The main peak at 285.3 eV was assigned to carbon atoms bound to two hydrogen atoms (CH_2 ; aliphatic) and sp^3 -hybridized carbon atoms as in diamond-like carbon. The peak at 286.0 eV was assigned to carbon atoms bound to one hydrogen atom (CH) and present in structures like alcohol (C–OH) and amine (C–NR₂). Peak at 287.1 eV is typical of carbon atoms bound to nitrogen and oxygen corresponding to structures like nitriles and ketones or aldehydes, respectively. Peaks at 288.4 and 289.7 eV were assigned to carbon atoms bound to two oxygen atoms (e.g.,

ester, carboxylic acid). The N 1s levels (Fig. 3c) can be decomposed into three contributions appearing at 399.5, 401.0 and 403.5 eV. The two main peaks at 399.5 and 401.0 eV were assigned to nitrogen atoms present in structures like nitrile (CN), amine (NH₂) and oxime (C=N–O), respectively. At 403.5 eV nitrogen atoms involved into oxidized structures like nitro (NO₂) appears. The O 1s peaks (Fig. 3d) were decomposed into two components appearing at 532.7 and 533.9 eV and corresponding to oxygen atoms bound to carbon atoms found in functions like alcohol, ketone (COC), and carboxylic acid (COOH), respectively.

The bombardment of composite films induced the same modifications at the surface. XPS analysis revealed the depletion of N-species and incorporation of oxygen. Table 3 shows the relative atomic concentrations of C, N and O for irradiated composite films with 5 keV H⁺ (10¹⁶ at cm⁻²) and 10 keV H⁺ (10¹⁷ at cm⁻²).

Compared with irradiated PAN films, the presence of nanotubes provoked an increase in the percentage of carbon for 5 keV H⁺ irradiation, a more significant nitrogen elimination but with less incorporation of oxygen. These phenomena were amplified by the increase in the NTs content. The decomposition of the C 1s, N 1s and O 1s levels were realized with the same components as used for PAN films. At the surface, the presence of nanotubes seemed to not affect the structures created by the proton bombardment. The observed variations of relative atomic percentages throughout all the samples (with and without nanotubes) were probably induced during the transfer to the analysis instrument by exposure to the atmospheric oxygen.

TEM observations of the surface of irradiated composite films reveal some interesting modifications. Bombardments provoke major morphological changes in the depth range of ions. Fig. 4 shows

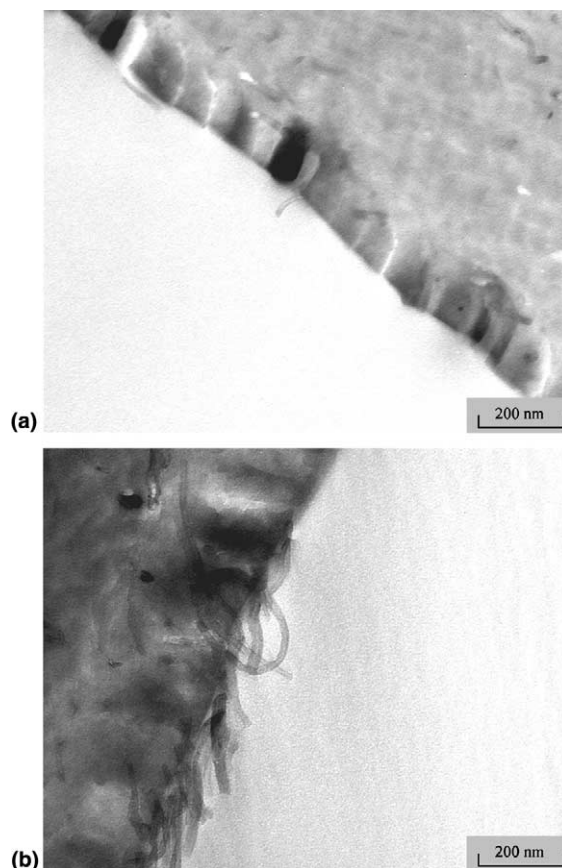


Fig. 4. Low resolution TEM images of the surface of composite films containing 4% of nanotubes and irradiated by protons beam. Irradiation conditions: (a) 5 keV H⁺, dose: 10¹⁶ at cm⁻²; (b) 10 keV H⁺, dose: 10¹⁶ at cm⁻².

Table 3

Relative atomic concentrations of carbon, nitrogen and oxygen for the irradiated PAN and composite films; 5 keV H⁺ (10¹⁶ at cm⁻²) and 10 keV H⁺ (10¹⁷ at cm⁻²)

	Carbon (%)		Nitrogen (%)		Oxygen (%)	
Proton beams (keV)	5	10	5	10	5	10
PAN films	81	85	7	5	12	10
Composite 1%	85	85	5	4	10	11
Composite 4%	84	85	5	4	11	11
Composite 10%	88	83	4	6	8	11

low resolution TEM images for composite films containing 4% of nanotubes and irradiated with 5 keV H^+ (Fig. 4a) and 10 keV H^+ (Fig. 4b) and for a dose of 10^{16} at cm^{-2} . The bombardment led to the emergence of the nanotubes outside of the organic film. Moreover, in the depth range of the ions, the polymer shows drastic morphological modifications. The structure appears like a lamellate or fringe structure. The thickness of this structure was similar to the calculated range of the protons in the polymer. We observe a depth of around 100 and 200 nm for 5 and 10 keV H^+ , respectively.

From these first results, it is possible to infer on some aspects of the reactivity of polyacrylonitrile-nanotubes composite films under irradiation with protons. At the surface, outgasing of entire nitrile groups ($-CN$) occurs, leaving carbon rich top layers which are probably unsaturated since the irradiated spots turn slightly brownish. These unsaturated and unrelaxed layers are responsible for the incorporation of oxygen by reaction with atmospheric oxygen. The XPS elemental analysis data were in agreement with IR results (Fig. 5) observed in previous works [13,14]. Due to the presence of enamionitrile structures shown by band at 2190 cm^{-1} , it is conceivable that they are formed at a deeper distance in the film. The unrelaxed or reactive state of the matter along the ions

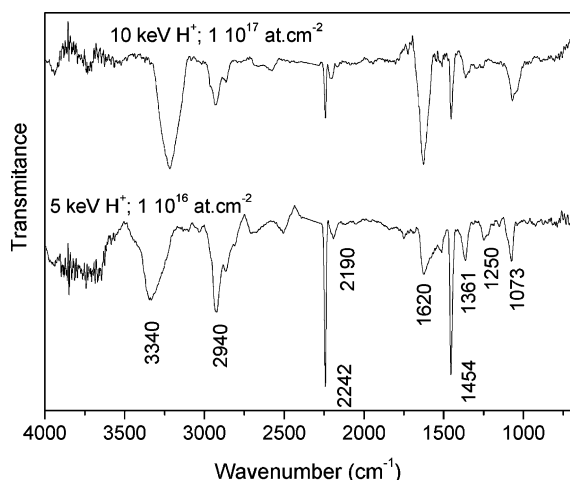


Fig. 5. IRRAS spectra of irradiated PAN films. Irradiation conditions: 5 keV H^+ , dose: 10^{16} at cm^{-2} ; 10 keV H^+ , dose: 10^{17} at cm^{-2} .

trajectories can create structures like amine, oxime and/or amide (broad band at 3340 and 1620 cm^{-1}) by interacting with protons and/or oxygen.

The presence of carbon nanotubes in the film led to lower relative concentration of nitrogen and oxygen at the surface but the same types of structures as in PAN films were created. For thin composite films, the thickness reduction disappears when 10% of nanotubes are present. For thick composite films, the emergence of NTs was observed. This shows that the NTs are not destroyed when subjected to a proton beam.

4. Conclusions

The results presented here are the first of a research that we have initiated on the influence of carbon nanotubes in polymer films when they are bombarded with proton beams. We have observed that changes induced in the film are related to the irradiation conditions. The bombardment of the composite films induces the emergence of the nanotubes outside of the polymer but with no increase of the surface roughness. Spectroscopic modifications in both pristine PAN and in composite PAN/MWNTs films are globally similar: the most significant feature being a lower relative concentration of nitrogen with respect to carbon close to the surface in the latter case. In the future, we intend to study the reactivity and the stability of the composite films in different atmospheres at various temperatures.

Acknowledgements

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